MOVPE Growth Studies of Mn−incorporated GaInAs / InP Layers

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I. Introduction

III−V compound semiconductors−based diluted magnetic semiconductor (DMS) alloys or hybridization between ferromagnetic materials and III−V compound semiconductors using their magneto−optical characteristics, e.g. Faraday or Kerr effects, are very promising for magneto−optical device applications in photonic integrated circuits (PICs). This is because such III−V magnetic semiconductors can be monolithically integrated on the present PICs fabricated by III−V compound semiconductors. So far, the most intensively investigated III−V DMS materials were (GaMn)As and (InMn)As / GaAs grown by low temperature molecular beam epitaxy (LT−MBE). [1−3] Using such LT−MBE growth technologies, device structures for waveguide−type optical isolators utilizing MnAs nano−clusters have been proposed recently. [4] However, though metal−organic vapor phase epitaxy (MOVPE) is one of the most important technologies for the fabrication of highly integrated PICs, there were nevertheless only a few reports on MOVPE growth of III−V DMS materials. [5−7] It was reported that, in the MOVPE growth of magnetic semiconductors related to Mn−incorporated GaAs layers, MnGaAs cluster structures were normally formed in GaAs host matrices. [5, 7] In order to fabricate highly integrated PICs for optical communication systems, InP−related materials are mainly used and will be in future. Some investigations of (GaInMn)As alloy materials grown by LT−MBE have been recently reported as the first results based on InP−related materials. [8, 9] In this paper, MOVPE growth studies of Mn−incorporated (GaIn)As layers on InP substrates are demonstrated. Surface morphologies and magnetic properties for Mn−incorporated (GaIn)As / InP layers are investigated as a function of MOVPE growth conditions.

II. Experimental Procedures

A horizontal low−pressure MOVPE system was used at a reactor pressure of 50 mbar (37.5 Torr). Triethylgallium (TEGa) and trimethylindium (TMIn) were used as group III source materials, and tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) as group V source materials, respectively. As manganese organometallic precursor, bis−(methylcyclopentadienyl) manganese ($(MeCp)_2Mn$) was used at a temperature of 20 ºC. The partial pressure of $(MeCp)_2Mn$ for growth of Mn−incorporated layers was calculated using the estimated vapor pressure of 0.05 mbar (0.038 Torr) at 20 ºC. Typical nominal Mn / (III + Mn) ratios in the vapor phase, x, which are the ratio of partial pressure of manganese sources to the total one of organometallic source materials, were 0.04 and 0.08. The layer structures of the Mn−incorporated (GaIn)As / InP samples were undoped InP cap / Mn−incorporated (GaIn)As / undoped InP / undoped (GaIn)As etching stop layers / undoped InP buffer (referred to as TYPE−A) and Mn−incorporated (GaIn)As / undoped (GaIn)As / undoped InP / undoped (GaIn)As etching stop layers / undoped InP buffer (referred to as TYPE−B) on (100) Fe−doped InP S.I.−type substrates, as shown in Fig. 1. In order to discuss the dependence of Mn incorporation into (GaIn)As layers on MOVPE growth conditions, the V / (III + Mn) ratio and the growth temperature dependence of Mn−incorporated (GaIn)As layers was investigated. Typical V / (III + Mn) ratios were chosen from 15 to 120, and growth temperatures (Tg) ranged from 350 to 500 ºC.

X−ray diffraction (XRD) measurements were carried out to investigate structural properties of the Mn−incorporated (GaIn)As layers. The surface morphologies of Mn−incorporated (GaIn)As layers were observed by scanning electron microscope (SEM). Their magnetic properties were characterized by superconducting quantum interference device (SQUID) magnetometers. Magnetic fields were applied in a direction parallel to the substrates plane, here ***H***//[011] and ***H***//[0−11].

III. Results and Discussion

A summary of the growth condition, such as V / (III + Mn) and Tg, dependence of surface morphologies for Mn−incorporated (GaIn)As layers is shown in Fig. 2. Typical SEM images of the samples are also shown. Solid circles numbered in the figure represent the samples grown under the condition that Mn / (III + Mn) ratios in the vapor phase, x, equal to 0.04. It is found that surface morphologies of the samples strongly depend on V / (III + Mn) ratios and Tg. Under low V / (III + Mn) ratio and low Tg conditions, a whisker growth occurs (the dark gray region in the figure). A whisker growth tends to be mostly inhibited under the growth conditions in the boundary zone in the figure (the light gray region and dashed lines). To prevent such anomalous growth of Mn−incorporated (GaIn)As layers under high Mn partial pressure and low Tg conditions, higher V / (III + Mn) ratios are needed. This is presumably caused by the solubility limit of Mn atoms into (GaIn)As layers and the lower thermal decomposition rates of TBAs and TBP at these extremely low Tg. When the Mn / (III + Mn) ratio in the vapor phase is increased from 0.04 to 0.08, the boundary zone of the growth conditions in which a whisker growth occurs is shifted toward the direction shown by black arrows in the figure. There are no apparent differences of the surface morphologies between TYPE−A and B samples. In XRD measurements for TYPE−A and B samples, XRD spectra from Mn−incorporated (GaIn)As layers are weak and broad and, in addition, tend to be shifted toward the higher angular (tensile) side of (400) reflections from the reference samples of undoped (GaIn)As layers, although it has not been indicated yet that the broadening of the XRD spectra is attributed to clusters formation in the Mn−incorporated (GaIn)As layers.

The magnetic properties of TYPE−A layers grown at 500 ºC as characterized by SQUID magnetometers are depicted in Fig. 3. Magnetic fields were applied in a direction parallel to the substrates plane, here ***H***//[011]. The nominal Mn / (III + Mn) ratio in the vapor phase, x, was around 0.08. It is found that, although diamagnetic characteristics of the undoped (GaIn)As and, in particular, the InP substrate are dominant, a hysteresis loop indicating ferromagnetic coupling is observed at 5 K. When magnetic fields are applied in a direction parallel to [0−11], no ferromagnetic characteristics is observed in TYPE−A layers. Figure 4(a) shows magnetic characteristics of TYPE−B at 5 K. The nominal Mn / (III + Mn) ratio in the vapor phase, Tg, and the direction of applied magnetic fields were the same as those of TYPE−A in Fig.3. In contrast to the TYPE−A layer structures, TYPE−B layers show much strong ferromagnetic characteristics. A hysteresis loop is observed more clearly for the applied magnetic field direction of [011] as compared to the direction of [0−11] in TYPE−B layers.

The temperature dependence of remanent magnetization, $\boldsymbol{M_r}$, for TYPE−B characterized in Fig. 4(a) are summarized in Fig. 4(b). Here, $\boldsymbol{M_r}$//[011] ($\boldsymbol{M_r}$//[0−11]) means remanent magnetization in a direction parallel to [011] ([0−11]) after the application of magnetic fields in the respective direction. It is found that $\boldsymbol{M_r}$ values in [011] direction are around three times larger than those in [0−11] direction, and that the Curie temperature, Tc, is more than 300 K. These results indicate that Mn−related cluster structures are formed in the Mn−incorporated (GaIn)As layers grown at 500 ºC. The magnetic easy axis of the clusters tended to be aligned in a direction parallel to [011] rather than [0−11]. This means that, if clusters with NiAs−type hexagonal crystalline structures, such as Mn(Ga)As or MnAs layers, are formed also in Mn−incorporated (GaIn)As layers, the a−axis of the clusters is oriented parallel to the [011] direction.

At the Tg below 450 ºC, on the other hand, Mn−incorporated (GaIn)As layers show diamagnetic behavior (mainly for TYPE−A with x = 0.08 or 0.04). In TYPE−A samples and Mn−incorporated GaAs layers grown using AsH_3 and PH_3 as group V source materials, it was reported that at lower growth temperatures higher saturation magnetization were found, and that ferromagnetic characteristics were observed up to around 300 K. [7] In Ref. 7, TYPE−A layers showed much stronger ferromagnetic coupling than TYPE−B when the magnetic fields were applied in a direction parallel to [011]. This tendency is different from the one shown in Figs. 3 and 4. In TYPE−A layers grown using AsH_3 and PH_3 in Ref. 7, it was confirmed by cross−sectional transmission electron microscopy (TEM) that Mn(As)P clusters were formed in undoped InP cap layers on Mn−incorporated (GaIn)As layers grown at around 450 ºC due to surface segregation of Mn atoms. Therefore, it is assumed that surface segregation of Mn atoms in the (GaIn)As layers grown using TBAs is smaller as for layers grown using AsH_3.

IV. Summary

The V / (III + Mn) ratio and the growth temperature dependence of Mn−incorporated (GaIn)As layers grown by MOVPE on InP substrates and the magnetic characterizations is demonstrated. To prevent a whisker growth in Mn−incorporated (GaIn)As layers under high Mn partial pressure and low Tg conditions, higher V / (III + Mn) ratios are needed. The Mn−incorporated (GaIn)As layers without undoped InP cap layers show stronger ferromagnetic coupling as compared to those with the InP cap layers. Ferromagnetic coupling is observed for temperatures even above room temperature.

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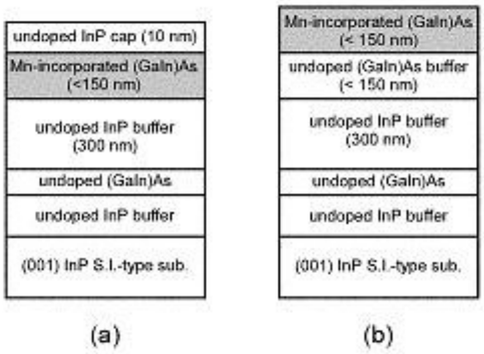

Fig. 1 Layer structures of Mn-incorporated (GaIn)As / InP samples (a) referred to as TYPE-A, and (b) as TYPE-B, respectively.

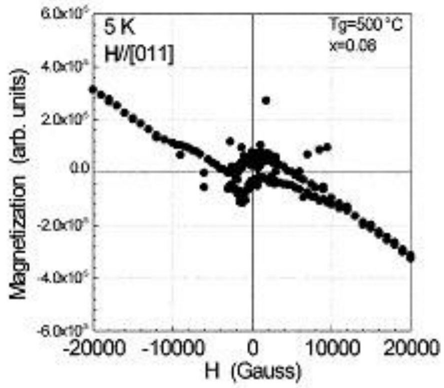

Fig. 3 Magnetic characteristics of undoped InP cap / Mn-incorporated (GaIn)As layers (TYPE-A) measured by SQUID magnetometers. Mn / (III + Mn) ratio in the vapor phase, x, was 0.08 and the growth temperature, Tg, was 500 °C. Magnetic fields, H, were applied in a direction parallel to the substrate plane, here H//[011].

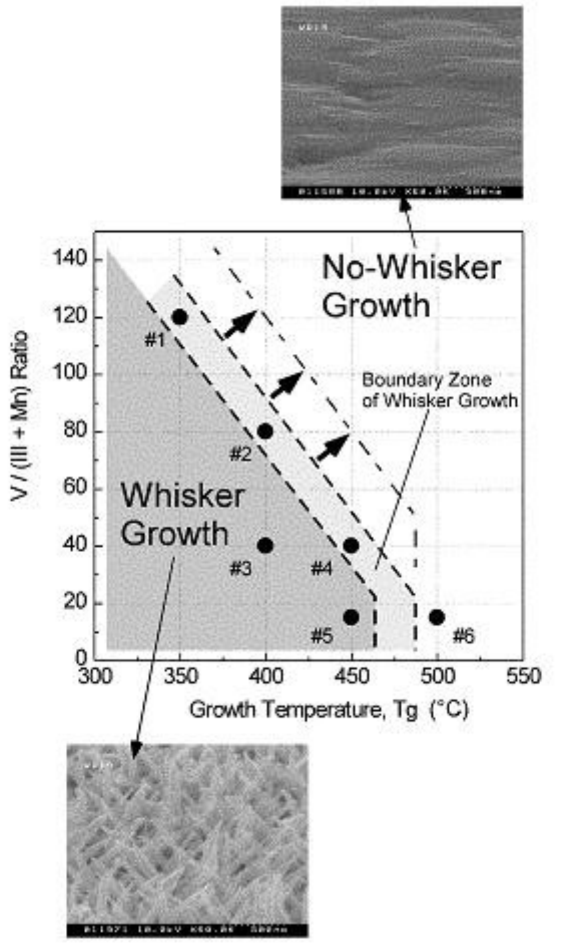

Fig. 2 Growth condition dependence of Mn-incorporated (GaIn)As layers. Solid circles numbered in the figure represent the samples grown under the condition that Mn / (III + Mn) ratios in the vapor phase, x, equal to 0.04. When the ratios, x, were increased from 0.04 to 0.08, the boundary zone of whisker growth was shifted to the direction indicated by black arrows. SEM images are the typical surface morphologies for the whisker and the no-whisker growth.

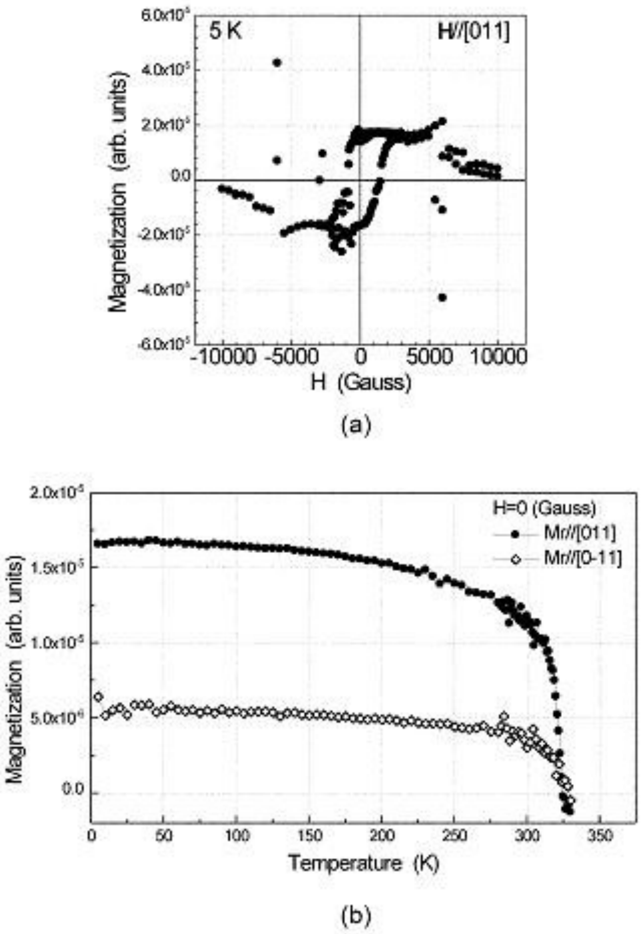

Fig. 4 (a) Magnetic characteristics of Mn-incorporated (GaIn)As layers (TYPE-B) measured by SQUID magnetometers. Mn / (III + Mn) ratio in the vapor phase, x, was 0.08 and the growth temperature, Tg, was 500 °C. Magnetic fields were applied in a direction parallel to the substrate plane, here H//[011]. (b) Temperature dependence of the magnetic characteristics. Remanent magnetizations, Mr, were measured in a direction parallel to the substrate plane, here Mr//[011] (solid circles) and [0-11] (open diamonds).